(19) Europäisch s Patentamt
European Patent Offic
Office européen d s brevets

(11) Publication number : 0 665 207 A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number : 95300475.1

(22) Date of filing : 26.01.95

(51) Int. Cl.[6] : C07C 43/04, C07C 31/10, C07C 41/01, C07C 29/145

(30) Priority : 28.01.94 US 188007

(43) Date of publication of application : 02.08.95 Bulletin 95/31

(84) Designated Contracting States : DE FR GB

(71) Applicant : TEXACO DEVELOPMENT CORPORATION
2000 Westchester Avenue
White Plains, New York 10650-001 (US)

(72) Inventor : Knifton, John Frederick
10900 Catskill Trail
Austin, Texas 78726 (US)
Inventor : Dai, Pei-Shing Eugene
3437 Brittany
Port Arthur, Texas 77642 (US)
Inventor : Taylor, Robert Joel Jr.
4120 Sleepy Hollow Lane
Port Arthur, Texas 77642 (US)
Inventor : Martin, Bobby Ray
285 East Caldwood Drive
Beaumont, Texas 77707 (US)

(74) Representative : Watkins, David
Urquhart-Dykes & Lord
91 Wimpole Street
London W1M 8AH (GB)

(54) Isopropyl alcohol and ether production from acetone.

(57) A one-step method is disclosed for synthesis of ethers from acetone, which method compris s reacting an acetone-rich feed over a bifunctional catalyst comprising 5%-45% by weight hydrogenation catalyst on 55%-95% of the total catalyst weight of a support comprising a zeolite and a Group III or IV metal oxide.

EP 0 665 207 A1

This invention r lat s to a novel one-st p int grat d m thod for production of high octan blending components for reformulated gas line from acetone. The method is particularly adapted to the production of such blending components fr m a crude by-product acetone str am. Th m thod c mprises r acting th crud acetone stream over a bi-functional catalyst to give an effluent rich in diisopropyl ether (DIPE), methyl *t*-butyl ether (MTBE) and isopropyl *t*-butyl ether (IPTBE). Isopropyl alcohol is an intermediate product of the method and may be isolated, if desired.

The bifunctional (hydrogenation/etherification) catalyst comprises a hydrogenation catalyst on a support comprising a zeolite from the group consisting of β-zeolite, a medium-pore pentasil or Y-zeolite, and an oxide from Group III or IV of the Periodic Table.

It is known to those skilled in the art that ethers, including both symmetrical and unsymmetrical ethers, may be prepared by reacting an alcohol with another alcohol to form the desired product. The reaction mixture, containing catalyst and/or condensing agent may be separated and further treated to permit attainment of the desired product. Such further treatment commonly includes one or more distillation operations.

Hydrogenation catalysts are known and are generally selected from Group VIII of the Periodic Table. Suitable metals include, but are not limited to, platinum, palladium, tin, nickel and copper alone, or in combination.

In U.S. Patent No. 3,955,939 to Sommer et al. (1976), there is disclosed the production of a water-fr e mixture of isopropyl alcohol, diisopropyl ether and by-products by the catalytic hydration of propylene in the gaseous phase at temperatures of 140°-170°C, wherein the water-free mixture formed according to the process can be used directly as an additive to gasoline fuel.

In U.S. Patent No. 5,144,086, to Harandi et al., there is disclosed an integrated multistage process for the production of diisopropyl ether and substantially pure propene wherein in the second stage isopropanol containing about 0%-20% water is contacted with an acidic large pore zeolite etherification catalyst which comprises a β-zeolite having a Si:Al ratio of about 30:1 to 50:1.

Another group of molecular sieve zeolites which have been investigated for industrial application is pentasil zeolites. The pentasil family of zeolites contains a continuing series of which ZSM-5 and ZSM-11 are end m mbers. See T. E. Whyte et al. "Zeolite Advances in the Chemical and Fuel Industries: A Technical Perspective," CATAL. REV.-SCI. ENG., 24,(4), 567-598 (1982).

A good overview of applications for zeolites, including pentasil type zeolites is found in an article titled, "Zeolite Catalysts Face Strong Industrial Future", European Chemical News, 10 July, 1989, p. 23. For example, medium pore H-ZSM-5 is sometimes added to a zeolite Y catalytic cracking catalyst to increase the aromatics content and hence motor octane, of the gasoline fraction. In the limited space of ZSM-5, where two pore systems of about 5-6Å in diameter intersect to give spatial regions of around 9Å diameter at the intersections, th re is a cutoff around C_{10} to C_{11} for products from transformation of a wide range of feedstocks, including alkanes, olefins and alcohols.

In allowed U.S. Patent Application Serial No. 07/917,218, there is disclosed a method for preparing m thyl tertiary butyl ether by reacting butanol and methanol in the presence of a catalyst comprising a super-acid alumina or a faujasite-type zeolite.

None of the available references would seem to suggest the one-step conversion of low value crude acetone in a by-product stream into useful oxygenate products. The portion of said by-product stream which typically comprises acetone is about 20% to 80%. It would greatly enhance the economics of any process to produce MTBE or other oxygenates if acetone from a by-product stream could be converted in one step to us ful oxygenate products which could be fractionated to isolate diisopropyl ether (DIPE), methyl *t*-butyl ether (MTBE) and isopropyl *t*-butyl ether (IPTBE).

According to the present invention there is provided a one-step method for the generation of ethers from acetone, which method comprises reacting an acetone-rich feed over a bifunctional catalyst comprising:

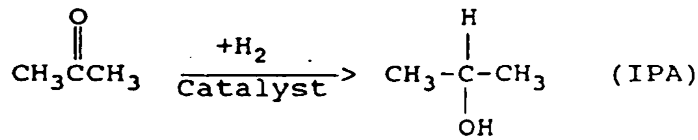
5%-45% by weight of a hydrogenation catalyst consisting essentially of one or more metals from the group consisting of nickel, copper, platinum, palladium, tin and chromium,

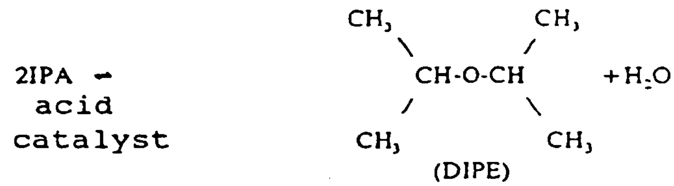
and 95 to 55% by weight of an etherification catalyst consisting essentially of a zeolite and at least one metal oxide selected from Groups III or IV of the Periodic Table, the relative proportions by weight of the zeolite and the metal oxide constituents falling within the range 5:95 to 95:5.

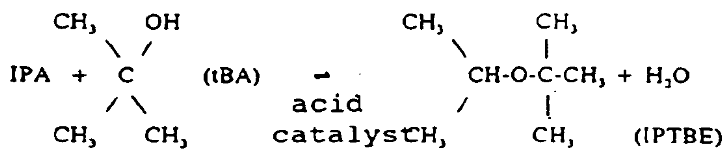
Preferably, the zeolite is selected from the group consisting of β-zeolites, pentasil zeolites and Y-zeolites.

In the production of high octane blending components for reformulated gasoline such as diisopropyl eth r (DIPE), methyl *t*-butyl ether (MTBE) and isopropyl *t*-butyl ether (IPTBE) by the method outlined above, the by-product aceton stream contains in addition significant quantities, that is, pref rably greater than 5% of both methanol (MeOH) and *t*-butanol (tBA). For the cogeneration of DIPE, MTBE and IPTBE, th crude ac t n feed preferably contains 10%-40% each of b th methanol and *t*-butanol.

The one-step synthesis can be represented by:







(Eq. 1)

In a process to make propylene oxide a large number of by-products are typically generated with the desired product. The by-products may include formic acid, acetic acid, *t*-butanol and acetone. The acetone may constitute about 20% to 80% of certain crude by-product streams. These crude acetone streams may be further mixed with methanol.

In related art, it is known to produce IPA and DIPE by the hydration of propylene and subsequent etherification of IPA. The instant invention allows the production of IPA and DIPE as well as other ethers such as MTBE and IPTBE from crude acetone containing *t*BA and MeOH in one-step in the presence of a bifunctional catalyst and hydrogen. The bifunctional catalyst comprises 5%-45% by weight hydrogenation catalyst consisting essentially of one or more metals from the group consisting of nickel, copper, platinum, palladium, tin and chromium on 55% to 95% of the total catalyst weight of a support consisting essentially of a zeolite and an oxide of Group III or IV of the Periodic Table.

The total proportion by weight of the portion of the catalyst comprising a hydrogenation catalyst is preferably between 5 wt% and 40 wt%. A preferred combination of metals for the hydrogenation portion of the catalyst is nickel and copper, where the total metal content of Ni/Cu is in the range of 8 wt% to 40 wt% and preferably 25% to 35%. The catalyst contains a nominal loading of nickel between 20 wt% and 30 wt%, preferably 15%-30% and particularly about 28%, and a nominal loading of copper of 2 wt% to 15 wt%, preferably about 4%.

In some cases it is useful to include chromium with nickel and copper, as demonstrated in Example 4 below. When present, a chromium proportion of about 1 wt% to 5 wt% is appropriate, preferably about 2 wt%.

The etherification portion of the catalyst preferably comprises 5%-95% by weight of β-zeolite or medium-pore pentasil zeolite or Y-zeolite and 95%-5% of an oxide of Group III or IV. With respect to the etherification portion of the catalyst, the zeolite preferably comprises 5% to 65% by weight and the metal oxide comprises 95% to 35% by weight. Example 1 below demonstrates the use of a Ni-Cu hydrogenation catalyst on a support comprising 10% by weight β-zeolite and 90% alumina, while Example 2 below demonstrates 50% β-zeolite and 50% alumina.

It appears that the zeolites which are most useful for the etherification portion of the bifunctional catalyst are large pore zeolites, such as, for example, β-zeolite or medium pore pentasil zeolites, i.e., those having a pore size of greater than about 5.5 Å.

Zeolite beta is a crystalline aluminosilicate having a pore size greater than 5 Å. The composition of the zeolite, as described in U.S. Patent No. 3,308,069, in its as-synthesised form may be expressed as follows:

$$[XNa(1.0\pm0.1-X)TEA]AlO_2\cdot YSiO_2\cdot WH_2O$$

where X is less than 1, preferably less than 0.7; TEA represents the tetraethylammonium ion; Y is greater than

5 but less than 100; and W is up to about 60 (it has be n found that the degr of hydration may be higher than originally determined, where W was defin d as being up to 4), depending on the degr f hydration and the m tal cation present. Th TEA component is calculat d by diff rences from the analyzed value of sodium and the theoretical cation to structural aluminium ratio of unity.

In the fully base-exchanged form, zeolite beta has the composition:

$$[(X/n)M(1\pm0.1-X)H]AlO_2 \cdot YSiO_2 \cdot WH_2O$$

where X, Y and W have the values listed above and n is the valence of the metal M. This form of the zeolite may be converted partly to the hydrogen form by calcination, e.g. at 200°C to 900°C or higher. The completely hydrogen form may be made by ammonium exchange followed by calcination in air or an inert atmosphere such as nitrogen.

The preferred forms of zeolite beta are the highly acidic, high silica forms, having silica-to-alumina m l ratio of at least 10:1, and preferably in the range of 10:1 to 50:1 in the as-synthesised form, and a surface area of at least 100 m^2/g.

Suitable β-zeolites for the practice of this invention include Valfor C806β, Valfor CP815β and Valfor C861. Valfor® is the registered trademark of the PQ Corporation.

Valfor® C806β zeolite is zeolite beta powder in template cation form. It is a high silica shape selective z o-lite which contains the organic template used in the crystallization step, having been isolated after filtration and washing of the synthesis product. C806β has a SiO_2/Al_2O_3 molar ratio of 23-26; the crystal size is 0.1-0.7 um; the surface area after calcination is about 700-750 m^2/g; the cyclohexane adsorption capacity after calcination is 19-24g/100g; Na_2O content is about 0.01-1.0% by weight anhydrous; and, the organic content is about 11-13% by weight, on a water-free basis.

Valfor® C815β zeolite is a calcined zeolite beta powder in hydrogen, sodium form. It is similar to C806β except the product has been calcined to decompose the organic template. C815β is a high silica, shap selective aluminosilicate with a large pore diameter. C815β also has a SiO_2/Al_2O_3 molar ratio of about 23-26; the crystal size, surface area, cyclohexane adsorption capacity and Na_2O are all within the same ranges as giv n for C806β.

Also, very effective in the bifunctional catalyst is the isostructural group of medium-pore pentasil zeolites.

An article titled "Molecular Sieve Catalysts," by J. Ward, Applied Industrial Catalysis, Vol. 3, Ch. 9, p. 271 (1984) provides an overview of the structure of pentasils. These zeolites, as well as silicalite have SiO_2-Al_2O ratios greater than 10. Silicalite is an inorganic molecular sieve described in U.S. Patent No. 4,061,724, incorporated herein by reference in its entirety. Silicalite usually has a Si:Al ratio greater than 200. Silicalite, ZSM-5, ZSM-11 and related materials have structures with ten-ring channel systems in contrast with the eight-membered zeolites such as A and erionite and the twelve-membered systems such as zeolites X and Y.

Pentasil zeolites are hydrophobic compared with A, X and Y zeolites. ZSM-5 has orthorhombic unit cells, whereas ZSM-11 is tetragonal.

The pentasil structures are very thermal and acid stable. They are synthesised in the presence of ammonium ions, which become an integral part of the structure. Heating up to 600°C decomposes the organic cations leaving the highly porous structure.

The channel size of pentasil materials is intermediate between, for example, small pore erionite and large pore zeolite Y.

Other ZSM series zeolites are not considered to be pentasils. ZSM-21, ZSM-35 and ZSM-38 are considered to be of the ferrierite type zeolite. ZSM-20 is considered of the faujasite type and ZSM-34 is considered to be of the offretite/erionite group.

Medium pore, pentasil-type zeolites having 10-membered oxygen ring systems include, for example, ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-48 and laumontite. Their framework structures contain 5-membered oxygen rings and they are more siliceous than previously known zeolites. In many instances these zeolites may be synthesised with a predominance of silicon and with only a very small concentration of other atoms such as aluminium; thus, these zeolites may be considered as "silicates" with framework substitution by small quantities of other elements such as aluminium. Among the zeolites in this group, only ZSM-5 and ZSM-11 have bidirectional intersecting channels, the others have nonintersecting unidirectional channels.

The medium-pore pentasils, unlike other zeolites, have pores of uniform dimension and have no larg supercages with smaller size windows. This particular feature is believed to account for their unusually low cok -forming prop nsity in acid-catalyz d r actions. B cause th p ntasil zeolit s are dev id f th bottl -n cks in the window/cag structur , molecul s larg r than the siz of the channel do not form with th exception perhaps at the intersections.

The preferr d forms of p ntasil z olite are the highly acidic, high silica forms, having silica-to-alumina mol ratio of at least 30:1, and preferably in the range of 30:1 to 350:1 in the as-synthesised form. A narrower range of 50:1 to 150:1 is preferred and the pentasil zeolites demonstrated in the examples possess SiO_2/Al_2O_3 ratios

of about 31:1 to ca. 350:1.

Said z olite eth rification catalysts ar formed in the pr s nce of a binder, such as Group III or Group IV m tal oxide. The zeolites are combined with the bind r by a variety of f rming techniques. Th Group III r Group IV oxid s used in conjunction with said β-zeolite include oxid s f aluminium, silicon, titanium, zirconium, hafnium, germanium, tin and lead, as well as combinations thereof. Alumina is preferred. Said binders may comprise as much as 10% to 90% of the formed catalyst.

Said metal oxide may optionally be further modified with a halogen, a halogen-containing organic compound, or a halogen-containing acid. Said halogen may be fluorine, chlorine, bromine or iodine, but is preferably fluorine. In the case of fluoride treatment, the fluoride content of the treated β-zeolite may be in the rang of 0.1 to 10 wt%, but preferably is about 1%. Said fluoride-treated zeolites may optionally be calcined, at temperatures of 200°C and above, prior to further usage or modification.

Another type of zeolite which is useful in the etherification portion of this integrated catalyst generally comprises dealuminised Y-zeolite catalysts.

The zeolites to use in the dealuminised form for the reaction of Eq. 1 are certain crystalline aluminosilicate zeolites, particularly the isostructural group of faujasite zeolites that include the synthetic X- and Y-zeolites, of which the Y-zeolites are preferred.

The unit cells of faujasite zeolites are cubic, $a_o \approx 2.5$ nm, and each contains 192 silicon- or aluminium-centered oxygen tetrahedra which are linked through shared oxygen atoms. Because of the net negative charge on each of the aluminium-centered tetrahedra, each unit cell contains an equivalent number of charge-balancing cations. These are exclusively sodium ions in zeolites in their synthesised form. Typical cell contents for the Y-zeolites in the hydrated form are:

$$Na_{56}[(AlO_2)_{56}(SiO_2)_{136}]_x \cdot 250\ H_2O$$

Y-zeolites are distinguished on the basis of the relative concentration of silicon and aluminium atoms and the consequent effects on detailed structure and related chemical and physical properties. The aluminium atoms in the unit cell of Y-zeolite vary from 76 to 48, resulting in a Si:Al ratio between 1.5 and 3.0. Both th cation concentration and charge density on the aluminosilicate structure are lower for Y-zeolites than f r X-zeolites, where the aluminium atoms in the unit cell vary from 96 to 77.

Preferably, said Y-zeolites are dealuminised by ammonium exchange followed by calcination, or by treatment with ethylenediaminetetraacetic acid (EDTA) or other chelating agents or by treatment with fluorine or a fluorine-containing compound such as silicon tetrafluoride or ammonium fluorosilicate, or hydrothermal treatment and/or acid treatment. Said dealuminised Y-zeolites should have a silica-to-alumina molar ratio of greater than three, preferably a ratio of 5 or greater and most preferably a silica-to-alumina ratio of 5 to 100. The examples demonstrate the usefulness of catalysts having a silica-to-alumina ratio of 5 to 50 and particularly 15 to 30.

Examples of suitable commercially available dealuminised Y-zeolites include UOP's LZY-82 and LZY-72, PQ Corporation's CP-304-37 and CP-316-26, UOP's Y-85, Y-84, LZ-10 and LZ-210.

The unit cell size and SiO_2/Al_2O_3 molar ratio for typical dealuminised Y-zeolites are noted in the table below:

ZEOLITE TYPE	UNIT CELL SIZE (Å)	SiO_2/Al_2O_3 MOLAR RATIO
LZY-82	24.53	7.8
LZY-85	24.49	9.1
LZY-10	24.32	23.7
LZY-20	24.35	18.9
LZY-84	24.51	8.4
LZ-210	24.47	9.9
LZY-72	24.52	8.1
CP316-26	24.26	45.7

Particularly effectiv in the subject cogeneration f MTBE, IPTBE and DIPE are the β-ze lites containing metal oxide carriers.

Said catalysts may b in the form of powders, pellets, granules, sph res, shapes and extrudates. Th examples describ d h rein d monstrate the advantages of using extrudat s.

The r action may be carried out in either a stirred slurry react r or in a fixed bed continuous flow reactor.

The catalyst c ncentration should be sufficient to provide the desired catalytic effect.

Hydrogenation/etherification to DIPE, MTBE or ITPBE can g nerally be conduct d at temperatur s from 20° to 250°C; the preferr d range is 50° to 200°C. Good r sults are bserv d thr ughout this t mperature range. However, it can be noted that the best conversion figures for MTBE, DIPE cogeneration are observed when the temperature is 210°-290°F (99°-143°C). The total operating pressure may be from 0 to 5000 psig (0.1 to 35 MPa), or higher. The preferred pressure range is 100 to 1000 psig (0.8 to 7 MPa).

Typically, IPA and DIPE are generated continuously in up to ca. 98 wt% concentration or greater in the crude liquid product at total liquid hourly space velocities (LHSV) of up to 10 or higher and relatively mild conditions, where:

$$\text{LHSV} = \frac{\text{Volume Of Total Liquid Feed Run Through The Reactor Per Hour}}{\text{Volume of Catalyst In Reactor}}$$

Conversions of acetone are estimated in the following examples using the equation:

$$\frac{(\text{Mole\% of Acetone in Feed} - \text{Mole\% of Acetone in Product})}{\text{Mole\% of Acetone in Feed}} \times 100$$

In the examples which follow it is noted that:

(1) Acetone is almost completely converted to IPA (major product) as well as small amounts of 2-m thyl pentane and unknown alcohol.

(2) In Example 1, optimum selectivity to DIPE (15.4%-15.9%) was achieved at the reaction temperature of about 284°-289°F (140°-143°C). Temperatures greater than 290°F (143°C) appear to be detrimental to the combined yields of the desired products (IPA + DIPE) and tend to promote the dehydration reaction of IPA to propylene, leading to the formation of large amounts of gas products.

(3) In Example 2, over the temperature range of 210°-264°F (99°-129°C), the DIPE yield increases with increasing temperature.

(4) A comparison between Example 2 and Example 1 for the DIPE yields at each comparable temperature indicates that the higher the β-zeolite content, the greater the DIPE yield. Up to 20% of selectivity to DIPE was attained in Example 2 at 264°F (129°C). The combined yields of IPA and DIPE reach a maximum value of 96.2% at 246°F (119°C).

(5) The results clearly demonstrate that high yield of IPA and DIPE can be generated from the hydrogenation of pure acetone over one Ni/Cu catalyst on a β-zeolite/alumina support. The total metal content of Ni+Cu is in the range of 8 to 40 wt%, and the atomic ratio of Ni/Cu is in the range of 1:1 to 10:1. The β-zeolite content in the support ranges from 5-95%.

The following examples are merely illustrative of the preferred embodiment. Many variations thereon may be made without departing from the spirit of the disclosed invention, as will be evident to those skilled in the art.

EXAMPLE 1

A 32% Ni/Cu on 10% β-zeolite catalyst was prepared by impregnating a support containing 50g of 10% β-zeolite/90% alumina support with a 40 cm³ aqueous solution containing 51g of nickel nitrate hexahydrate and 5.4 grams of copper nitrate hemipentahydrate. The impregnated support was dried at 250°F (121°C) for 2 hours and then calcined at 600°F (315°C) for 4 hours. The calcined support was impregnated again with 37 ml of an aqueous solution containing 51g of nickel nitrate hexahydrate and 5.4g of copper nitrate hemipentahydrate. The impregnated support was dried at 250°F (121°C) for 2 hours and then calcined at 900°F (482°C) for 8 hours.

Catalyst screening runs were performed in a microreactor test unit which has two reactors in series s parated by a quench zone. The reactors were operated in a downflow configuration. The top reactor was loaded with a 4 cm³ catalyst. The second reactor has two catalyst beds of 4 cm³ of catalyst each separated by a 4 cm³ bed of inert material. The total charge of catalyst was 12 cm³ in the unit. Internal thermocouples were p sitioned at the bottom of each catalyst bed. The liquid feed was charged to the unit using a high pressure pump and the hydrogen was metered through a mass flow controller. Both hydrogen and liquid feedstock were mix d and charged to the unit. The molar ratio of hydrogen to acetone is about 0.5:1 to 30:1, preferably about 1:1 to 3:1. For the purpose of simplifying the analysis of liquid products by GC, pure acetone was used as a feedstock to demonstrate the chemistry involved in the instant invention.

The catalyst of Example 1 was activated by heating slowly from room temperature to 600°F (315°C) ov r an 8 hour period und r flowing nitrogen at 70 psig (0.5 MPa). The unit pr ssure was then rais d t 500 psig (3.5 MPa) with hydrogen and the catalyst b d was held at 600°F (315°C) for 12 hours und r fl wing hydrog n. Th catalyst bed was cooled d wn to bel w 200°F (93°C). The technical grad acetone (97% purity) was charged t the unit at 1 LHSV and 500 psig (3.5 MPa). The hydrogen fl w rate was contr lled to give a hydrog n to acetone mole rati of 5:1. The reacti n temperatur was varied from 210°F t 325°F (99°C to 163°C). The

liquid product was coll cted periodically in a chill d receiver at 0°F and 300 psig (2.1 MPa). Th product was analyzed by GC to determine the composition of hydrocarbon and oxygenates, and by Karl-Fischer titration for the water content.

The results of th analysis of liquid products are summarised in Tabl 1.

TABLE I

EXAMPLE 1: CATALYST - 32% Ni/Cu on 10% β-Zeolite support

Cut No.	Elapsed time (Hours)	Average Temp (°C)	Liquid Recov. (wt%)	Relative proportions of constituents (wt%)					
				C_3	Acetone	IPA	DIPE	C_6/C_9	Water
040	17	101	99	0.9	0	97.4	0.5	0.5	0.9
070	23	113	98	1.8	0	94.6	1.9	0.5	1.1
090	29	130	100	0.5	0.1	89.6	6.6	0.9	2.4
110	35	143	93	6.8	0.1	71.4	14.6	1.8	5.1
130	41	140	98	2.5	0.1	75.1	15.1	2.5	4.8
150	47	143	82	18.8	0.2	64.6	8.2	3.6	4.6
170	53	163	80	22.1	0.2	49.2	17.2	2.6	8.6

EXAMPLE 2

The catalyst of Example 2 was prepared by following th same procedur s as d scrib d abov for Exampl 1 xc pt th support used was a mixture f 50% β-z olit and 50% alumina.

The catalyst was activated and technical grade acetone was charged in the same manner as used in Example 1.

The result of the analysis of liquid products are summarised in Table II.

TABLE II

EXAMPLE 2: CATALYST - 32% Ni/Cu on 50% β-Zeolite support

Cut No.	Elapsed time (Hours)	Average Temp (°C)	Liquid Recov. (wt%)	Relative proportions of constituents (wt%)					
				C_3	Acetone	IPA	DIPE	C_6/C_9	Water
160	44	99	97	2.9	0	91.0	4.0	0.4	1.6
180	48	104	99	2.8	0	84.3	8.2	0.5	4.1
200	52	111	99	1.8	0	86.0	9.3	0.5	2.4
220	55	119	97	2.9	0.1	81.7	11.5	0.6	3.1
240	60	129	86	14.1	0.1	61.1	19.0	0.4	5.0

EXAMPLE 3

The catalyst f Exampl 3 was prepared by following the same proc dur s as d scribed abov for Example 1 exc pt th supp rt is a mixture of 60% β-z olite and 40% alumina.

The catalyst was activated and tested in the same manner as used in Example 1. The results of the analysis of liquid products are summarised in Table III.

The results show that, as the reaction temperature approached 256°F (124°C), up to 25 wt% of selectivity to DIPE was attained, and the combined yields of IPA and DIPE was 89.8 wt%.

TABLE III

EXAMPLE 3: CATALYST - 32% Ni/Cu on 60% β-Zeolite support

Cut No.	Elapsed time (Hours)	Average Temp (°C)	Liquid Recov. (wt%)	Relative proportions of constituents (wt%)					
				C_3	Acetone	IPA	DIPE	C_6/C_9	Water
Run A									
600	10	96	100	0	0	91.5	4.6	1.5	2.4
Run B									
600	4	115	100	0	0	90.4	5.4	1.5	2.6
700	8	127	100	0.3	0	63.2	20.7	1.0	14.9
Run C									
500	7	124	100	0.3	0	65.0	24.8	1.8	7.9

EXAMPLE 4

The catalyst of Example 4 is used to illustrat the application of a medium-p re pentasil zeolit , ZSM-5, in this process. Th catalyst was pr pared by using a support (8162CT91) comprising a 80 wt% f ZSM-5 zeolite having a silica/alumina mole ratio of 223 and 20 wt% of alumina. 50 grams of the dried support was impregnat d with 35 cm³ of a solution containing 11.4 grams of copper nitrate, 2.2 grams of nickel nitrate and 4.4 grams f chromium nitrate. The impregnated support was dried at 250°F (121°C) for 2 hours and calcined at 600°F (315°C) for 2 hours and 800°F (427°C) for 4 hours. The resulting catalyst contained 7 wt% CuO, 2 wt% CrO_3, and 1 wt% NiO.

The catalyst was activated and tested in the same manner as used in Example 1. The results of the analysis of liquid products are summarised in Table IV. The results show that, at 219°F, the combined yields of IPA and DIPE of 92.5 wt% and about 10 wt% DIPE were obtained using a ZSM-5 zeolite-containing catalyst.

TABLE IV

EXAMPLE 4: CATALYST - Cu/Cr/Ni on 80% Silicalite support

Cut No.	Elapsed time (Hours)	Average Temp (°C)	Liquid Recov. (wt%)	Relative proportions of constituents (wt%)					
				C_3	Acetone	IPA	DIPE	C_6/C_9	Water
100	10	104	100	1.8	0	82.7	9.8	1.3	4.5

Claims

1. A one-step method for the generation of ethers from acetone, which method comprises reacting an acetone-rich feed over a bifunctional catalyst comprising:
   5 - 45% by weight of a hydrogenation catalyst consisting essentially of one or more metals from the group consisting of Ni, Cu, Pt, Pd, Sn and Cr, and
   95 - 55% by weight of a support comprising an etherification catalyst consisting essentially of a zeolite and at least one metal oxide selected from Groups III or IV of the Periodic Table, the relative proportions by weight of the zeolite and the metal oxide constituents falling within the range 5:95 to 95:5.

2. A method as claimed in claim 1 wherein the acetone-rich feed additionally contains at least 5% by w ight of both methanol and *t*-butanol.

3. A method as claimed in claim 1 or claim 2 wherein the zeolite in the etherification catalyst is a β-zeolite.

4. A method as claimed in claim 3 wherein the β-zeolite content in the catalyst support ranges from 5% by weight to 95% by weight.

5. A method as claimed in claim 1 or claim 2 wherein the zeolite in the etherification catalyst is a pentasil zeolite.

6. A method as claimed in any preceding claim wherein the hydrogenation catalyst consists essentailly of nickel and copper.

7. A method as claimed in claim 6 wherein the hydrogenation catalyst also includes 1% to 5% by weight of chromium.

8. A method as claimed in any preceding claim wherein the Group III or Group IV metal oxide is selected from the group consisting of alumina or silica alumina.

9. A method as claimed in any preceding claim wherein the temperature ranges from 50°C to 200°C.

10. A method as claimed in any preceding claim wherein the hydrogen pressure ranges from 0.8 MPa to 7 MPa.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 30 0475

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
D,A	US-A-5 144 086 (M. N. HARANDI) * claims *	1-10	C07C43/04 C07C31/10 C07C41/01 C07C29/145
A	US-A-4 296 263 (G. R. WORRELL) * column 2, line 46 - column 6, line 40 *	1-10	
A	US-A-3 829 510 (R. T. ADAMS) * column 3, line 74 - column 4, line 21; claims *	1-10	
A	EP-A-0 323 138 (MOBIL OIL) * claims; examples 1-4 *	1-10	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C07C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 April 1995	Wright, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document